DESIGN AND DEVELOPMENT

OF SILVER-CADMIUM STORAGE BATTERIES

Final Report

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PURPOSE

To improve the power output per unit weight of a power supply for an orbiting vehicle, the development of a sealed silver oxide-cadmium battery was initiated. This battery development contract specified the requirement of a basic five ampere-hour cell capable of cycling for one year at a cyclic frequency of 100 minutes. In addition to cycling, other testing and support development work had to be performed. Basically, the other major phases of work which were performed are:

1. The improvement of seals to eliminate or minimize leakage during cycling and stand.

2. Separation evaluation studies to improve the cyclic life of a sealed silver oxide-cadmium cell.

3. Minimize the magnetic properties of the cell.

4. Establish the dynamic testing levels for the cell design.

5. Improve the power output per unit weight.

6. Determine the operating characteristics and activated stand characteristics of the cell at various temperatures.

7. Perform tests to evaluate the couple for extended overcharge periods and to establish the operating pressure as a function of the overcharge current.

I. INTRODUCTION

During this contractual period, cell design has progressed from the cylindrical cell to the prismatic or rectangular cell. The rectangular cell is more advantageous in that the separated core lends itself more readily to final inspection than does the cylindrical cell core. Also, the method of separation of the rectangular cell protects more efficiently against internal shorting. It is also felt that the rectangular cell core lends itself more readily to overall battery configuration as well as controlled mass production.

Difficulty was encountered in the effort to minimize the magnetic properties of the cell. However, all materials presently being used in the fabrication of test cells have minimum magnetic properties and have been proven suitable for long cyclic operation.

The five ampere-hour silver oxide-cadmium cell should be capable of cycling for one year at a 100 minute cyclic frequency and ten percent depth of discharge when temperatures are controlled between 20° and 80° F. At the end of the contract period, two sealed silver oxide-cadmium batteries were cycling at the conditions prescribed by the NASA Contract NAS5-1318. The two tests, which are being conducted, are as follows:

1. A 10% depth of discharge at 80° F at an absolute pressure of less than 100 microns. The battery had completed 1841 cycles at the end of the contract period.

2. A 10% depth of discharge at 20° F at normal atmospheric pressure. The battery had completed 2155 cycles at the end of the contract period.

To better evaluate the performance of the silver-cadmium system when subjected to very deep discharges, another cyclic test is being conducted. This test consists of a five ampere-hour discharge over a two hour period, and an 18 hour charge at a constant voltage of 1.50 volts per cell with the current limited to 2.0 amperes. Since the original capacity of these cells was approximately six ampere-hours and with some capacity loss during the initial cycling, this test consists essentially of a 100% depth of discharge. The test is being conducted at 80° F and normal atmospheric pressure and had completed 154 cycles at the end of the contract period.

II. FACTUAL DATA

A. Cell Design

1. Original Charged Plate Construction

One of the limiting factors of the utilization of charged plates in cell construction is the sloughing action of cadmium during formation. Because of this sloughing action, much of the active material is lost during formation, and poor plate production is a result. Therefore, the amount of active material that can be uniformly deposited and insure good plate formation is limited. Since the amount of active material that can be uniformly deposited is limited, a greater amount of thin plates must be used in cell construction, thus increasing the relative amount of inactive material such as grid and separator.

Another difficulty encountered in the use of charged plates in cell construction is in balancing the active materials to obtain an equivalent overbalance of cadmium being necessary to guard against the evolution of hydrogen. Since varying cadmium plate efficiencies occur under present formation methods, it would be difficult to maintain proper active material balances for obtaining maximum power output.

Initial cell construction utilized cylindrical "D" size container. The power output of the rectangular cell is not as great as that of a cylindrical cell of comparable volume in small sized cells. Because of the space required for the inner retainer, terminal spades, and tabs, full utilization of the rectangular container volume is not possible. This space amounts to about 25% of the total volume. In the cylindrical container, nearly full utilization of the volume is possible with more than 90% of its volume being available for use. The power output of the nominal five ampere-hour cylindrical cell is approximately 1.75 watt-hours

per cubic inch, while for the similarly rated rectangular cell, the power output is 1.65 watt-hours per cubic inch.

Several reasons exist for the transition from the cylindrical to the rectangular cell container. One such reason is that the rectangular cell lends itself more efficiently to good packaging procedures. Also, the separated core of the rectangular cell lends itself more readily to good production methods and final inspection than does the separated cylindrical core. Because of the rolling operation involved in the construction of the cylindrical core, the use of uncharged plates is not suitable for good cell performance and cyclic life. When rolling the uncharged plates, cracking and sloughing of the active material occurs, thereby reducing cell performance and increasing the possibility of internal shorting. Therefore, it has been necessary to use charged plates in the construction of the cylindrical core.

Also, when charged plates are used in cell construction, the positive plates are charged to the divalent oxide voltage level. Since silver is a noble metal, its ion has great tendency to be reduced and, in this respect, it is a very good oxidizing agent. Because of the severe oxidation potential at the positive plate, the separator material deterioration, cyclic life is decreased when charged plates are used in cell construction or when the cell is operated at the higher oxidation state of silver.

2. Uncharged Plate Construction

The monovalent silver oxide-cadmium system appears to have a greater potential for achieving long cyclic life. Apparent advantages that the monovalent silver oxide-cadmium system has for achieving long cycle life are as follows:

a. Operating a positive plate at its lower state of oxidation should extend separator life due to its lower oxidation potential.

b. Since the oxidation of silver to the monovalent state is exceptionally efficient, the cell should operate at a low internal pressure.

c. Maintaining the positive plate at the lower state of oxidation would increase the plate's matrix structure, thus minimizing the shedding of active materials.

d. By controlled charging, an extremely fine discharge voltage control can be achieved.

A definite advantage of the monovalent silver oxide-cadmium system is that recharging can be accomplished very efficiently. In most instances, the recharge efficiency approaches 100%. Figure No. 19 is a graph of the input and output capacity of a ten cell battery that is being operated at the capacity of monovalent silver oxide. The battery is cycling automatically at a 100 minute frequency. During the 63rd cycle, 0.52 ampher-hour was removed from the battery in the 40 minute discharge time, and 0.54 ampere-hour was replaced in the 60 minute charging period with no loss in capacity in subsequent cycles. This output to input ratio shows an operating efficiency of 96.5%.

Since the oxidation of silver to the monovalent state is exceptionally efficient, a high recharge efficiency can be maintained throughout prolonged cycling.

By utilizing uncharged plates in cell construction, plate manufacturing is greatly simplified. The formation of plates prior to cell fabrication is no longer necessary, thereby decreasing the time required

for plate production. Plates of higher density can be used in cell construction, which allows more active material to be placed in a given volume. This, in turn, reduces the relative amount of inactive cell material such as grid and separator. The power output per unit weight of the cell is therefore improved. However, at higher discharge rates, the increase in current densities will cause lower cell voltage. The increased power output per unit weight is therefore made at the sacrifice of voltage at high discharge rates.

When forming the uncharged plates, voltage controls are maintained such that the charging rate will be reduced to milliamperes when the cell is at the capacity of the silver monoxide state. Since oxidation of silver to the monovalent state is exceptionally efficient, the cell operates at a low internal pressure. Because of the greatly reduced internal cell pressure, sealing of the cell can be accomplished more efficiently for long cyclic operation. Also, separator life should be extended due to the lower oxidation potential of the positive plate when operating at the monovalent oxide voltage level, thus extending cell life.

3. Optimum Cell Design

In order to minimize the magnetic properties of the cell, the container is drawn from Type 321 stainless steel. From the available containers, one was chosen whose size was adequate to produce the necessary five ampere-hours. The dimensions of the container are as follows:

Outside Length	1.469 ± .010 inches
Outside Width	0.781 ± .010 inches
Height	4.000 ± .010 inches
Wall Thickness	0.019 ± .003 inches

The container covers and terminals are also of 300 series stainless steel.

In the fabrication of the rectangular cell, four positive and five negative plates are used, the sizes of which are 1.25 by 3.00 inches. A ratio of negative to positive weight of 1.40 to 1.00 is utilized, consisting of 3.69 grams per square inch of negative active material and 3.30 grams per square inch of positive active material.

To separate the plates, two positive plates are laid end to end and wrapped with one layer of #9526 nylon nearest the plates, and four layers of #600 cellophane. The separated positive plates are folded together and a negative plate, which has one layer of R-35-D Viskon around it, is inserted between them. This method of separating plates minimizes internal shorting of the cell due to "sloughing" of active material and should add to the cycle life of the cell. These separated plates are then combined to form a cell core consisting of four positive and five negative plates.

After the cell core has been separated, the positive and negative tabs are crimped and spotwelded to form a single positive and single negative tab for the attachment of terminals. The tabs are then cut to length and inserted in the spade portion of the terminals. The spades are then crimped and spotwelded to complete the terminal connections.

The inner portion of the seal is attached to the cell core and the core is then placed in a cell container and the cover heliarc-welded to the container.

Before the outer portion of the seal is applied, the cell is activated with 28.0 cc of 1.303 specific gravity potassium hydroxide. After activation, the outer seal is applied and the cell is then completed. The average weight of the completed cell is 232.0 grams.

B. Seal Improvement

During this contractual period of work, two different seals were used in test cell fabrication. To facilitate the construction of test cells, a glass seal which was readily available was used in most initial fabrication. These seals were pressure tested prior to installation and again after all welding was performed on the cell. The glass-to-metal seal will perform well for very short intervals, but any long periods of cycling will completely destroy its ability to contain the potassium hydroxide electrolyte.

The second seal that was used was a compression type seal. The compression seal consists of three major components: A teflon inner retainer, a teflon o-ring between the inner retainer and cell cover and around the terminal, and a nylon outer retainer. The teflon inner retainer is constructed to serve a dual purpose, the first being to insulate the terminal from the cell container and cover. Secondly, it is constructed to assure that the terminal does not turn, which would cause shorting or severing of the tab-to-terminal connection. The o-ring is compressed between the terminal and the cover, thereby affecting a positive seal. This condition is aided by tapering the terminal hole in the cover. The nylon outer retainer is machined with a compression ring on one side. This ring is essential as it compresses the o-ring from the outer side and it also seals the terminal opening in the cover. Finally, Type AA Loctite is applied about the terminal to assure tightness of the seal.

The compression type seal cannot be classified as a hermetic seal, but appears to do a satisfactory job of containing the electrolyte and evolved oxygen. The leak rate of this type of seal has been measured

with a mass spectrometer at 1.1×10^{-7} cc of helium per second at a 15 psi differential. While this seal is far from the ultimate, it has proven superior to available glass seals.

A number of commercial manufacturers have been approached for the purpose of obtaining a ceramic seal that would be suitable for this operation. Several sample seals have been obtained and tested in an oxygen and KOH atmosphere. These initial tests, although not complete, have not disclosed a vastly superior ceramic seal.

C. Separation Evaluation

The life of a sealed silver-cadmium element will be governed primarily by the ability of insulating materials to retard the transfer and deposition of silver, either in the separator or on the negative plate. The fact that silver is a noble metal, its ion has great tendency to be reduced and, in this respect, it is a very good oxidizing agent. It has become apparent that a good separator material must have the following requirements:

1. Ability to withstand the severe oxidation potential at the positive plate.
2. Of small enough pore size to retard the migration of silver, yet capable of limiting internal resistance to a minimum.
3. Capable of withstanding high and low temperatures without appreciable change in pore volume.
4. Stable in potassium hydroxide over a wide range of temperatures.
5. Of sufficient pore volume to hold the amount of electrolyte required to satisfy conditions for recombination

of cadmium and oxygen without undue effect to capacity efficiency.

6. Void of organic material which may be oxidized to carbon dioxide with subsequent formation of cadmium carbonate.

Because of the extreme length of time necessary to evaluate separator materials when subjecting complete assemblies to life testing, it was considered desirable to develop a method to accelerate breakdown of separator materials. Figure No. 20 shows a container and method of assembling designed to facilitate the testing of separator materials. Insulating materials that were evaluated were used in the assembly of a simple three-plate element of one positive and two negative plates. The assembly was clamped in a special holder whereby one outside negative plate was held tightly and covered completely with a plastic block. The other negative plate was held in place with a smaller plastic block such that part of the plate was exposed. In assembling, care was taken to assure that each cell was held by their blocks at the same pressure.

Eight of these three plate elements were assembled with various separator materials for the separation evaluation test. The cells were flooded with electrolyte. The separators used in the construction of these cells were as follows:

Cell No.	Wraps about Positive	Wraps about Negative
1	1 #9526 Nylon, 1 #133 Visking	1 #R-75-D Viskon
2	1 #9526 Nylon, 2 #133 Visking	1 #R-75-D Viskon
3	1 #9526 Nylon, 2 #600 Cello.	1 #R-75-D Viskon
4	1 #600 Permion, 2 #300 Cello.	1 #R-75-D Viskon
5	1 #9526 Nylon, 1 #133 Visking	1 #R-75-D Viskon
6	1 #9526 Nylon, 3 #600 Cello.	1 #R-75-D Viskon
7	1 #9526 Nylon, 3 #300 Cello.	1 #R-75-D Viskon
8	1 #9526 Nylon, 1 #300 Cello.	1 #R-75-D Viskon
	1 #133 Visking	1 #R-75-D Viskon

These cells were then placed on automatic cycling which consisted of 20 minutes discharge time and 40 minutes charge time. During the discharge portion of the cycle, 20 ampere-minutes were removed from the cell, and 34 ampere-minutes were replaced during charge. This amounted to 70% overcharge in each cycle.

Cell No. 2 failed after 949 cycles, and a "post mortem" of the cell revealed no visible shorts. Failure of the cell was attributed to the badly oxidized state of the separator. After 1768 cycles, the cells were placed on open circuit voltage stand for nine days. A check of the cell voltages after the stand period showed that cell No. 4, 6 and 8 still had an open circuit voltage of 1.42 volts. The open circuit voltage of the other cells had decayed to a maximum of 1.18 volts, thus indicating that shorting of various degrees had occurred.

The results of this test indicated that the RAI Permion separator (a polyethylene film) might be the most desirable of the separators. Therefore, subsequent cell fabrication utilized various combinations of

No. 300 Permion and cellophane as the barrier membrane. However, cycling tests showed a considerable loss of capacity over initial cycles and shorter cell life. Investigation of these cells indicated that the #300 Permion was not sufficiently retarding the migration of silver.

The limited testing of the RAI separation indicated that it is not superior to cellophane for normal temperature cell usage and has the disadvantage of being very costly. Therefore, all the latest test cells are fabricated using multiple layers of cellophane as the membrane separator. It is possible, however, that the RAI separators are better suited for use at temperatures in excess of 100° F.

D. Magnetic Properties

In an effort to minimize the magnetic properties, 300 series stainless steel was used wherever possible. This material has excellent nonmagnetic properties and is very easy to weld. The terminals used in all cell construction are machined from 300 series stainless steel, and the cans and covers are drawn from Type 321 stainless steel.

An expanded stainless steel grid was also obtained for possible use as the grid material in cell construction. However, excessive cold working of the material during the expanding process had hardened the material to such a degree that it was impossible to use. Attempts at annealing the grid in a standard inert gas furnace improved the handling characteristics of the material, but left a very hard oxide coating that was undesirable and very difficult to remove. Since none of the commercial special metals companies would guarantee an oxide free annealed grid, investigations into the procurement of other grid materials were made.

Two other grid materials were obtained which might possess suitable electrical conductivity and magnetic properties for this

particular application. These two materials were cupro-nickel and 18% nickel silver. The nonmagnetic properties of these materials were found to be excellent. However, the electrical resistivity of both materials was excessively high. This high grid resistance produced a noticeably lower voltage level during discharge of the test cells. It was decided, therefore, to use silver grids on both the positive and negative plates. However, in all cell fabrication, stainless steel plate tabs are used as connectors between the grid and the terminals. This prohibits the possibility of complete oxidation and subsequent failure of the current-carrying plate tabs which might occur if silver grid or wire was used.

All materials used in cell construction possess minimum magnetic properties which should be suitable for this particular application.

E. Dynamic Testing Performance

The final design of the rectangular cell appears to withstand the normal dynamic conditions which could be present during the launch phase of an orbiting vehicle. Both single cells and batteries have been subjected to vibration, shock and acceleration that is in excess to the normal range of requirements.

Both ten cell batteries and single cells were subjected to the following dynamic testing.

Vibration -

Frequency	G Force or Double Amplitude
5 to 20 cps	0.5 in.
20 to 500 cps	10 g
500 to 2000 cps	15 g

Shock -

Time in Each Plane	G Force
10 MS	100 G

Acceleration -

Time in Each Plane	G Force
15 Min	50 G
30 Min (Terminals out)	100 G

During all dynamic testing the cells were discharged at a rate of 0.75 amperes. There was no indication of any malfunction during all testing.

Post mortems, performed on cells that had been subjected to all of the tests mentioned above, revealed no physical damage of any type. Other cells of the same test group were cycled subsequent to the dynamic testing and performed satisfactorily with no apparent loss in capacity or cyclic capability.

F. Capacity and Weight Improvement

A sacrifice of power output per unit weight was made in the transition from the cylindrical "D" cell to the prismatic or rectangular cell. This was expected, in that more complete utilization of the cell volume can be accomplished in the cylindrical cell. The power output of the nominal five ampere-hour cylindrical cell is approximately 1.75 watt-hours per cubic inch, while for the similarly rated rectangular cell, the power output is approximately 1.65 watt-hours per cubic inch.

The change to the rectangular cell construction, however, enabled the use of higher density unformed plates. Through maximum utilization of the cell volume, a nominal five ampere-hour cell will produce

approximately 16 watt-hours per pound when cell operation is maintained at the monovalent oxide voltage level. However, operation of the same cell at the divalent oxide voltage will produce approximately 25 watt-hours per pound.

Since it appears that the monovalent silver oxide-cadmium system is more suitable for the long cyclic operation required for this application, utilization of the maximum power output per unit pound cannot be obtained. However, it is felt that basic research should be performed to better evaluate and compare the two basic silver-cadmium systems, expecially with respect to their maximum capabilities. It is more than conceivable that both systems have a definite place in the family of military power supplies.

G. Operation Characteristics

Since unformed plates are used in all cell construction, it is necessary to charge them to prepare the cell for operation. To properly develop the plates in the cell, it has been found that a minimum of five charge and discharge cycles are required to obtain maximum capacity. All cell formation has been accomplished by controlling the maximum voltage drop across each cell to 1.50 volts per cell. The maximum current that has been used for formation is 2.0 amperes and the current decreased as the cell voltage reaches 1.50 volts. Electroformation is accomplished with a Harrison Laboratories 855 B current limiting constant potential charger. The cells are considered charged or formed when the current decreases to a level below 50 milliamperes. The time interval required to obtain the original formation is usually about 16 to 20 hours. On each subsequent charge and discharge cycle, the capacity of the cells will increase slightly for the first five cycles and after that time,

level off at a constant ampere-hour output of approximately 6.5 ampere-hours. This capacity can be increased by allowing the cells to charge for longer periods of time. It has been found that allowing the cell to charge at 1.50 volts constant potential for approximately five days, the capacity of the cell can be increased to 9.5 ampere-hours thereby utilizing silver at its dioxide level.

Figure No. 21 is a typical charge curve for a ten cell battery at 80° F. Since only approximately 0.5 ampere-hour had been discharged from the battery, charging was accomplished in 60 minutes. Charging was accomplished, utilizing the Harrison Laboratories 855 B current limiting constant potential charger, limiting the current to 2.0 amperes and the voltage drop across the battery at 1.50 volts per cell. It is apparent from data presented in Figure No. 21 that the charge current decreases as the cell voltage increases.

Since the charge efficiency is very high at 1.50 volts constant potential charge, very little gas is evolved and internal pressure of the cell is usually very low.

Because of the limited number of plates that are used in the cell construction, the cell is designed for low discharge rates that are not in excess of three amperes. Figure No. 22 presents a typical discharge voltage curve of a nominal five ampere-hour discharged at 3.0 amperes and at 80° F. These data disclose that approximately 25% of the total discharge time occurred at the divalent oxide voltage. A divalent oxide voltage will occur over prolonged cycling, even though charging is controlled at a constant voltage of 1.5 volts per cell. A capacity of 6.75 ampere-hours is obtained, when the cell is discharged to an end voltage of 1.0 volt.

The nominal five ampere-hour cell should be capable of long cyclic life at normal operating temperatures. However, cyclic life of the cell is considerably decreased when temperatures in excess of 100° F occur. A typical charge and discharge curve for the nominal five ampere-hour cell at 120° F would be very similar to those revealed by curves at 80° F.

Cyclic tests have indicated that the cell should also be capable of long cyclic life at 20° F. A typical charge of the nominal five ampere-hour cell at 20° F would also be very similar to that revealed by curves at 80° F. However, a slight decrease in capacity might occur, because of the decrease in plate efficiency at lower temperatures.

H. Overcharge Evaluation

Initial investigations of sealed cells utilizing the maximum potential power of the divalent silver oxide revealed that several variables existed which would affect recombination during overcharge. It was found that the ratio of positive to negative active materials, their final state-of-charge prior to sealing, their degree of wetting with potassium hydroxide for reaction, ratio of cadmium to plate surface area, type grid metal and perhaps other variants will affect the speed of recombination.

Unless a relatively high rate of recombination can be achieved, excessive oxygen pressures occur even at low rates of charge. An improved rate of recombination can be achieved by increasing the area of cadmium plate and operating the cell is a semi-dry state. However, operation of the cell is a semi-dry state is incongruent with long cyclic life and high output per unit weight. To increase the available cadmium

area, a greater number of thin plates must be used, thus increasing the relative amount of inactive material such as grid and separator.

The monovalent silver oxide-cadmium system appears to have a greater potential for achieving long cyclic life. The oxidation of silver to the monovalent state is exceptionally efficient, and the cell will operate at a low internal pressure. Therefore, in the operation of a cell at the monovalent oxide capacity level by constant potential charging alleviates the necessity of a high recombination rate.

I. Environmental Testing

1. Cyclic Test at 10% Depth of Discharge, +20° F

One battery consisting of ten rectangular cells connected in series was subjected to cycling testing at a temperature of 20 ± 1° F. This test, which is being performed at atmospheric pressure and consists of removing 0.5 ampere-hour in a 40 minute time interval and charging at a modified constant current, constant voltage of 1.5 volts per cell for 60 minutes. At the completion of the contract period, this battery had completed 2155 cycles of charge and discharge with no indication of any cell failure or irregularity.

The battery is monitored daily and the end-of-charge and discharge cell voltages are recorded. The end-of-charge and end-of-discharge voltages have remained very consistent throughout the entire test as is apparent from data in Table No. XV. However, there has been a slight decrease in the operating voltage of the battery. Figure No. 23 is a plot of the discharge voltage of the battery during its initial discharge cycle and also, during its 1793 discharge cycle. From these discharge curves, it can be seen that there is a definite loss of divalent voltage over this limited number of charge and discharge cycles. This decay of

the divalent oxide voltage was anticipated since the charging of the cells is controlled at a voltage that is low enough to prohibit the formation of any appreciable amount of the higher oxide during these short charge intervals.

2. Cyclic Test at 10% Depth of Discharge 120° F

A battery consisting of 10 series connected rectangular type sealed silver-cadmium cells was subjected to cyclic testing at 120° ± 2° F. The test, which was conducted at atmospheric pressure, consisted of a 40 minute discharge and 60 minute charge. During the discharge interval, 0.5 ampere-hour was removed. The charge voltage was controlled at 1.50 volts per cell, or 15 volts for the entire 10 cell battery. Charging current is limited to a maximum of 2 amperes, with the current decreasing as the maximum battery voltage was reached.

During the life of the test, the end-of-charge and end-of-discharge voltages of each cell were recorded daily. Table No. XVI discloses the end-of-charge and discharge voltages as they were recorded. Charge and discharge voltages were found to vary greatly in some cells while others remained fairly constant throughout the test.

After completing 624 charge and discharge cycles, the end-of-charge voltage of cell no. 41 was very low and it was apparent that the cell had a small internal short. Because of this low cell voltage, the test was temporarily halted while cell no. 41 was removed from the battery package. While the cell was being removed from the battery, and the charge and discharge circuit readjusted, the battery was on open circuit stand at room temperature. After the battery had been on stand overnight at the room temperature, a routine check of the cell open circuit voltages was made. It was found at this time that the open circuit

voltage of one other cell was also low. A "post mortem" of the two minutely shorted cells revealed severe deterioration of the separators. It was decided at this time to leave the remaining cells on open circuit stand and to monitor the open circuit voltage periodically. The remaining cells were then "post mortemed" and a similar deterioration of the separator was noted.

The separation utilized in the construction of these cells consisted of four wraps of 600 cellophane and one wrap of RAI Permion 300. The inert separation next to the positive material was woven nylon. The "post mortem" revealed that while the cellophane had almost completely deteriorated, the Permion was still fairly strong but completely coated with silver, and electronically conductive when dry.

Figure No. 24 is a graph of battery voltage versus time for two discharges that were made during the cycling at 120° F. It can be noted that the decrease in divalent oxide voltage was much more rapid and occurred more rapidly than at 20° F.

3. Cyclic Test in Vacuum Chamber at 10% Depth of Discharge at 80° F

This test is being performed on a ten cell battery that was fabricated from unformed plates. The cells were formed and subjected to approximately ten conditioning cycles prior to the start of this test. The battery was placed in a vacuum chamber and the chamber connected to a mechanical vacuum pump. The absolute pressure that is maintained in the vacuum chamber is less than 100 microns of mercury absolute. The cyclic frequency of the battery is 100 minutes with a 40 minute discharge and a 60 minute charge. The depth of discharge is 10%, or an output of 0.5 ampere-hour. Daily recordings are taken on the cell end-of-charge and end-of-discharge voltage.

In Table No. XVII are recorded the end-of-charge and end-of-discharge voltages at various cycles. The Table shows that the charge and discharge cell voltages have remained quite consistent throughout the entire testing to date. It is felt that this consistency will continue until one cell begins to fail at which time the other cells will accept a greater charging voltage.

Figure No. 25 is a graph of the battery voltage versus time for the first and 1438th discharge of this battery. During the first discharge cycle, the entire battery voltage was maintained at the divalent oxide level. After 1438 cycles, the divalent oxide level of voltage has decreased to approximately 25% of the total discharge. This indicates that the charging time interval is not long enough to completely charge the battery. On the initial charge and discharge cycle, the output of the battery greatly exceeded that which could be replaced in the 60 minute charge interval. After 1438 cycles, the input was slightly larger than the output.

4. Cyclic Test at 100% Depth of Discharge, 80° F

To evaluate the silver-cadmium system from the standpoint of very deep depths of discharge, a cyclic test was started that would allow a discharge of five ampere-hours over a two hour period, and a recharge consisting of 18 hours of modified constant potential charging at 1.50 volts per cell. This test is being conducted at 80° F and at normal atmospheric pressures. Because of the extended time interval to complete a charge and discharge cycle, only limited information is available at this time.

In Table No. XVIII are recorded the end-of-charge and end-of-discharge voltages of each of the cells in the battery. While there has

been some slight variation in the end-of-charge voltage, and a slight decrease in the end-of-discharge voltage, as a whole the voltages have remained very constant.

Figure No. 26 is a graph of battery voltage versus time for the first and 54th discharge of this battery. These two curves show that the battery divalent oxide voltage has actually increased over these longer charging intervals. At the same time, the discharge voltage has decreased but only slightly.

The cells in this battery were fabricated from unformed plates. It is felt that the cyclic life of this battery will be a function wholly of the life of the separation. It is also fundamental that cycle life expectancy is an inverse function of depth of discharge. Consequently this battery, being discharged at approximately its full capacity, can be expected to have a significantly shorter cycle life when measured in number of cycles than a battery cycled at a 10% depth.

III. SUMMARY

Cell leakage has been minimized by the utilization of the compression type seal. Although this seal is not a true hermetic seal, it has been leak tested on a mass spectrometer, and its' leak rate was determined to be 1.1×10^{-7} cc of helium per second at a 15 psi differential. Various ceramic seals have been tested in a potassium hydroxide and oxygen atmosphere without any appreciable results being obtained. Investigations are still being made for the procurement of a ceramic seal capable of minimizing cell leakage for long cyclic life. At present, no ceramic seal has been found, which would be superior to the compression type seal.

Separation evaluation tests have been conducted to determine the separators to be used in cell construction. These tests consisted of eight three-plate elements, utilizing various separators which were subjected to automatic cycling. After prolonged cycling, the elements were placed on open circuit stand for approximately ten days. Of the eight elements tested, only three exhibited normal open circuit voltage after the stand period. From the separators used in these three elements, the separation to be used in cell construction was chosen.

The magnetic properties of the cell have been minimized through the selection of proper components. Series 300 stainless steel was used wherever possible because of its low magnetic properties. The magnetic properties of the cell should be suitable for this particular application.

Limited dynamic testing has been performed on both single cells and batteries that was in excess to the normal range of requirements. During all dynamic testing, the cells were discharged at a rate of 0.75

amperes. There was no indication of malfunction during testing, and "post mortems" of tested cells revealed no internal damage of any type.

The power output per unit weight of the five ampere hour cell has been improved by the utilization of higher density plates in cell construction, which reduced the relative amount of inactive materials such as grid and separators. Also, a more complete utilization of the cell volume has aided in obtaining greater power output per unit weight.

Several automatic and manual cyclic tests have been conducted to establish the operating characteristics of the five ampere-hour sealed silver oxide-cadmium cell at various temperatures. An automatic cyclic test was conducted at 120° F, and automatic cyclic tests are still being conducted at 20° F and 80° F. From these studies, charge and discharge characteristics of the cell were determined, along with other cell operating characteristics.

Some studies were performed to evaluate the couple for extended overcharge period. It was found that operation of the cell at the divalent oxide capacity level will produce high internal cell pressures unless a high rate of recombination can be achieved. However, operation of the cell at the monovalent oxide capacity level by constant potential charging does not require a high recombination rate.

IV. DISTRIBUTION OF ENGINEERING HOURS AND MATERIALS

The following is a list of engineering personnel and technicians associated with this contract, the hours of work performed by each, and the cost of materials purchased during the Fourth Reporting Period:

Name	Title	Hours
Morse, E.	Senior Engineering Supervisor	44
Sieglinger, F.	Project Engineer	159
Call, D.	Battery Engineer	508
Carr, D.	Technician	396
Kernohan, T.	Technician	280
		1387

Purchased Materials Cost ----------$ 1,330.29

APPENDIX

K&E 10 X 10 TO THE ½ INCH KEUFFEL & ESSER CO. 359-11 MADE IN U.S.A.

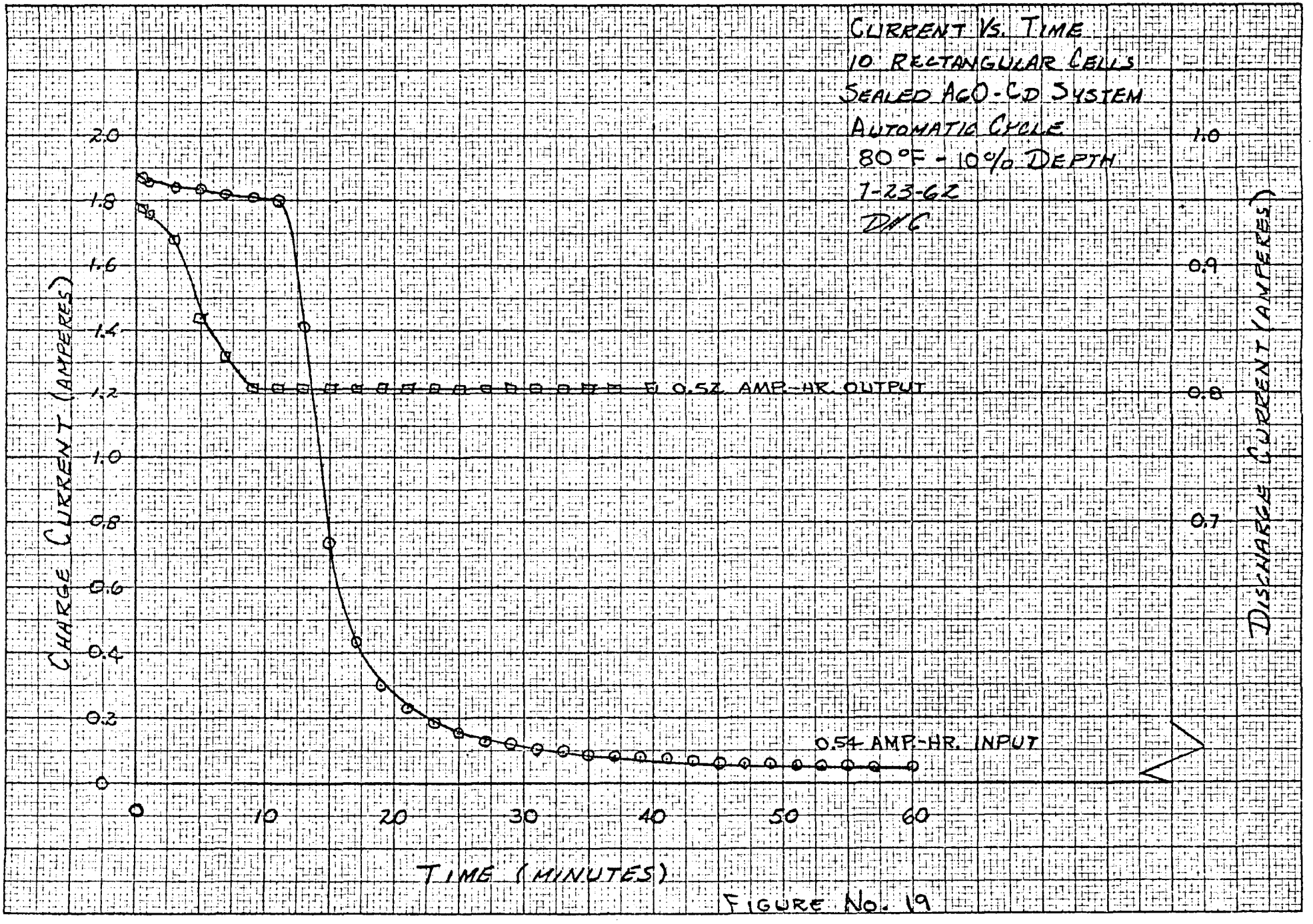

FIGURE No. 19

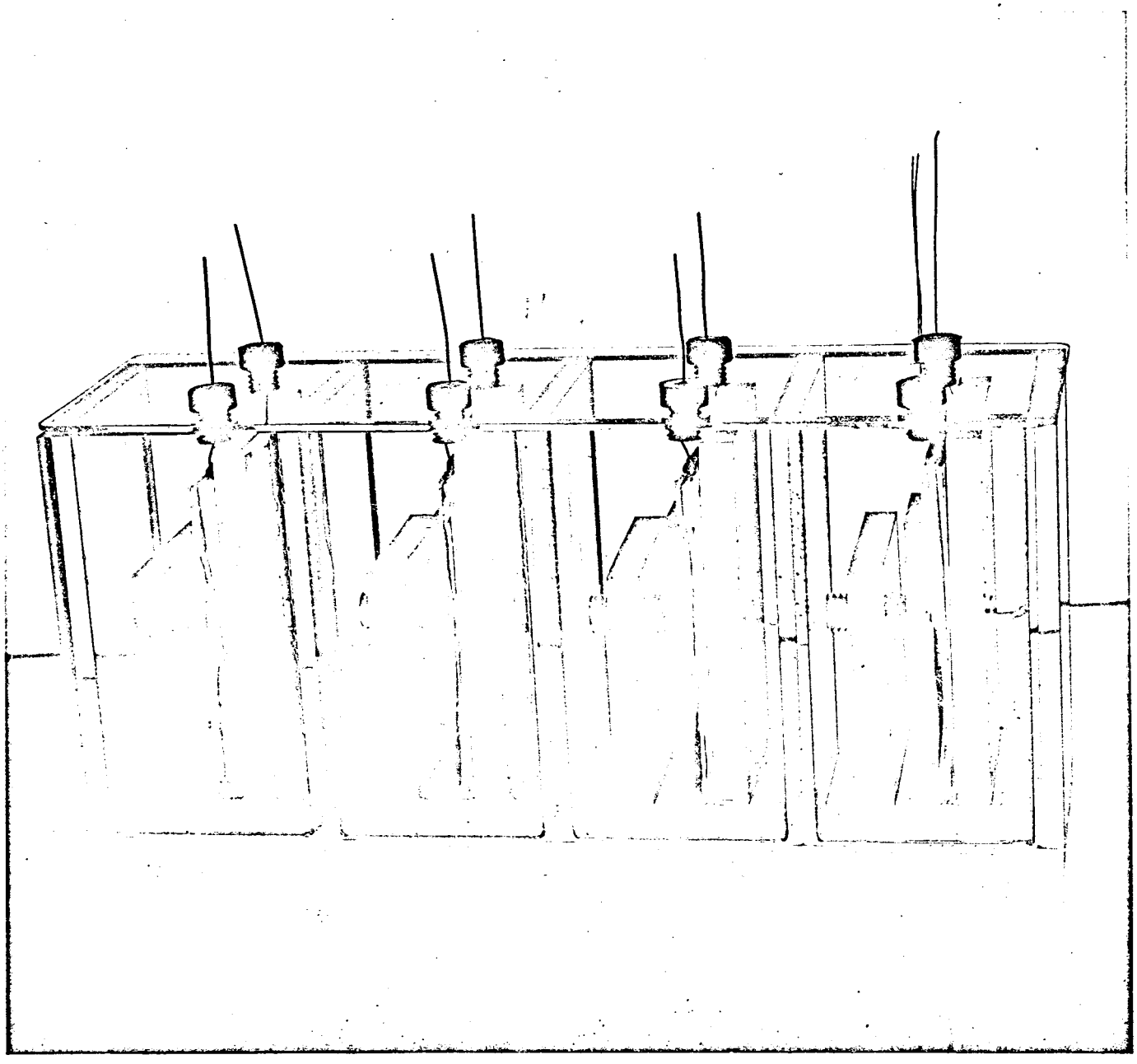

FIGURE NO. 20
Container and Assembly
For Separation Testing

K&E 10 X 10 TO THE ½ INCH 359-11
KEUFFEL & ESSER CO. MADE IN U.S.A.

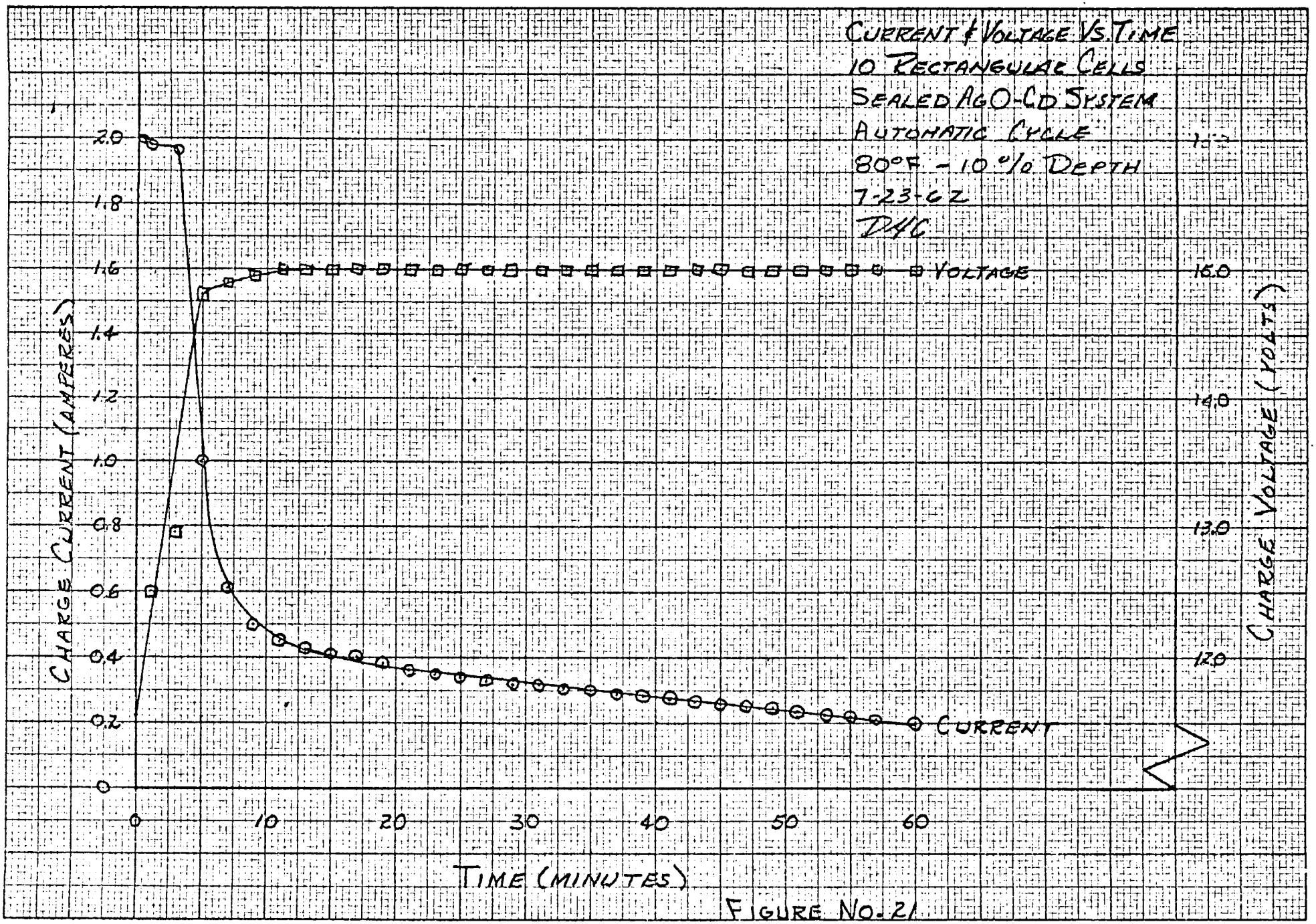

FIGURE NO. 21

K&E 10 X 10 TO THE ½ INCH 359-11
KEUFFEL & ESSER CO. MADE IN U.S.A.

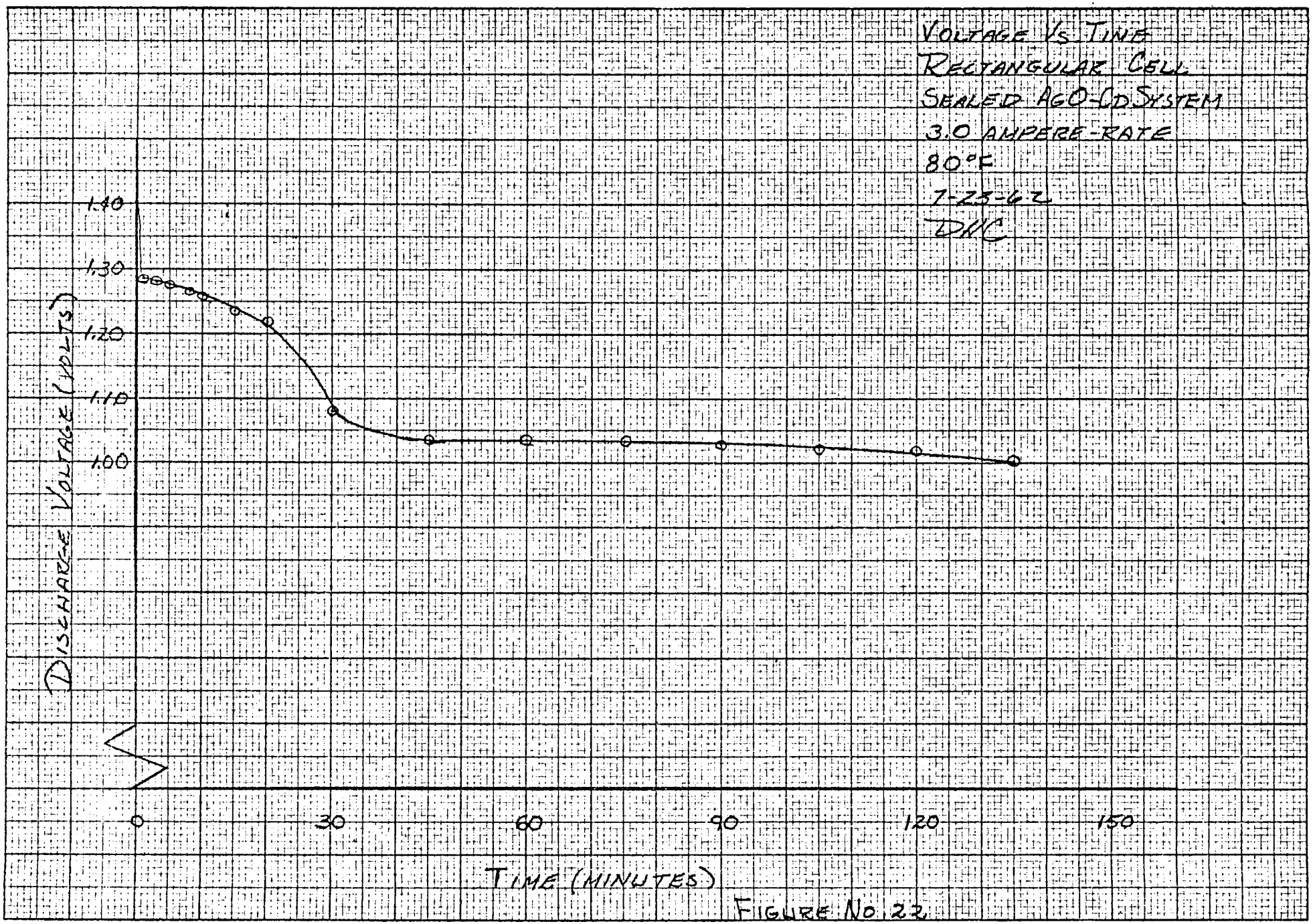

FIGURE NO. 22

K+E 10 X 10 TO THE ½ INCH 359-11
KEUFFEL & ESSER CO. MADE IN U.S.A.

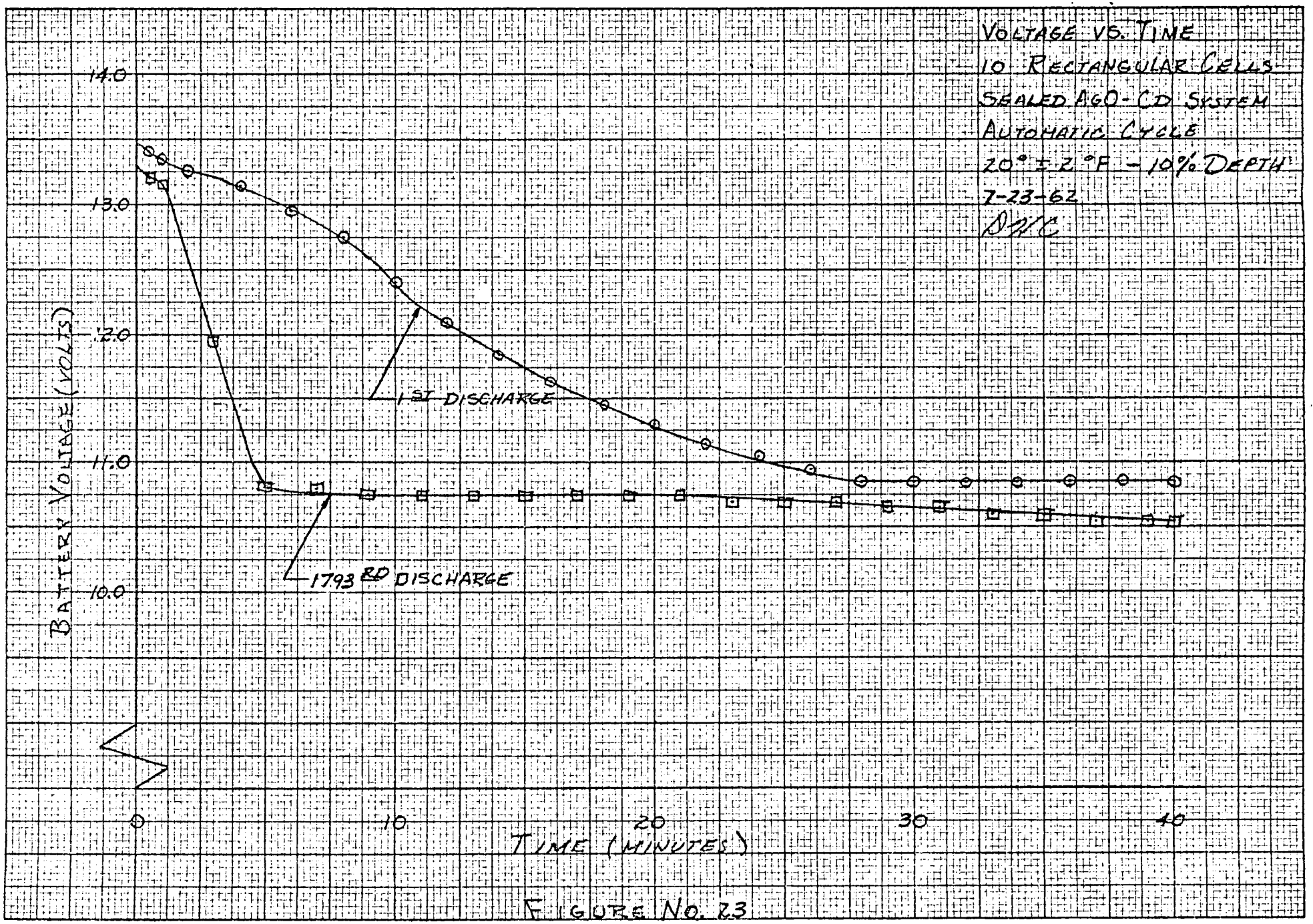

FIGURE NO. 23

K&E 10 X 10 TO THE ½ INCH KEUFFEL & ESSER CO. 359-11 MADE IN U.S.A.

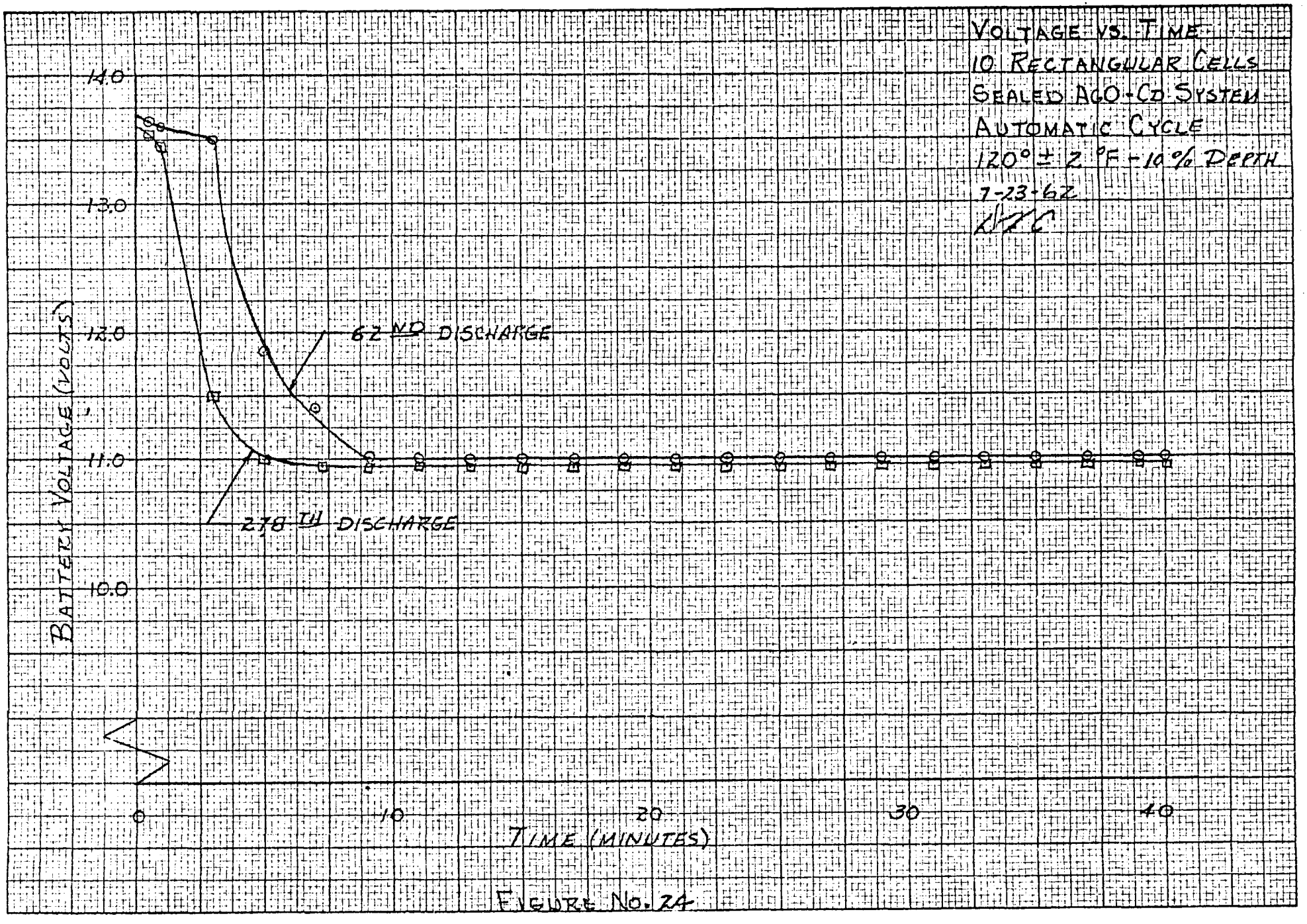

FIGURE No. 24

K+E 10 X 10 TO THE ½ INCH 359-11
KEUFFEL & ESSER CO. MADE IN U.S.A.

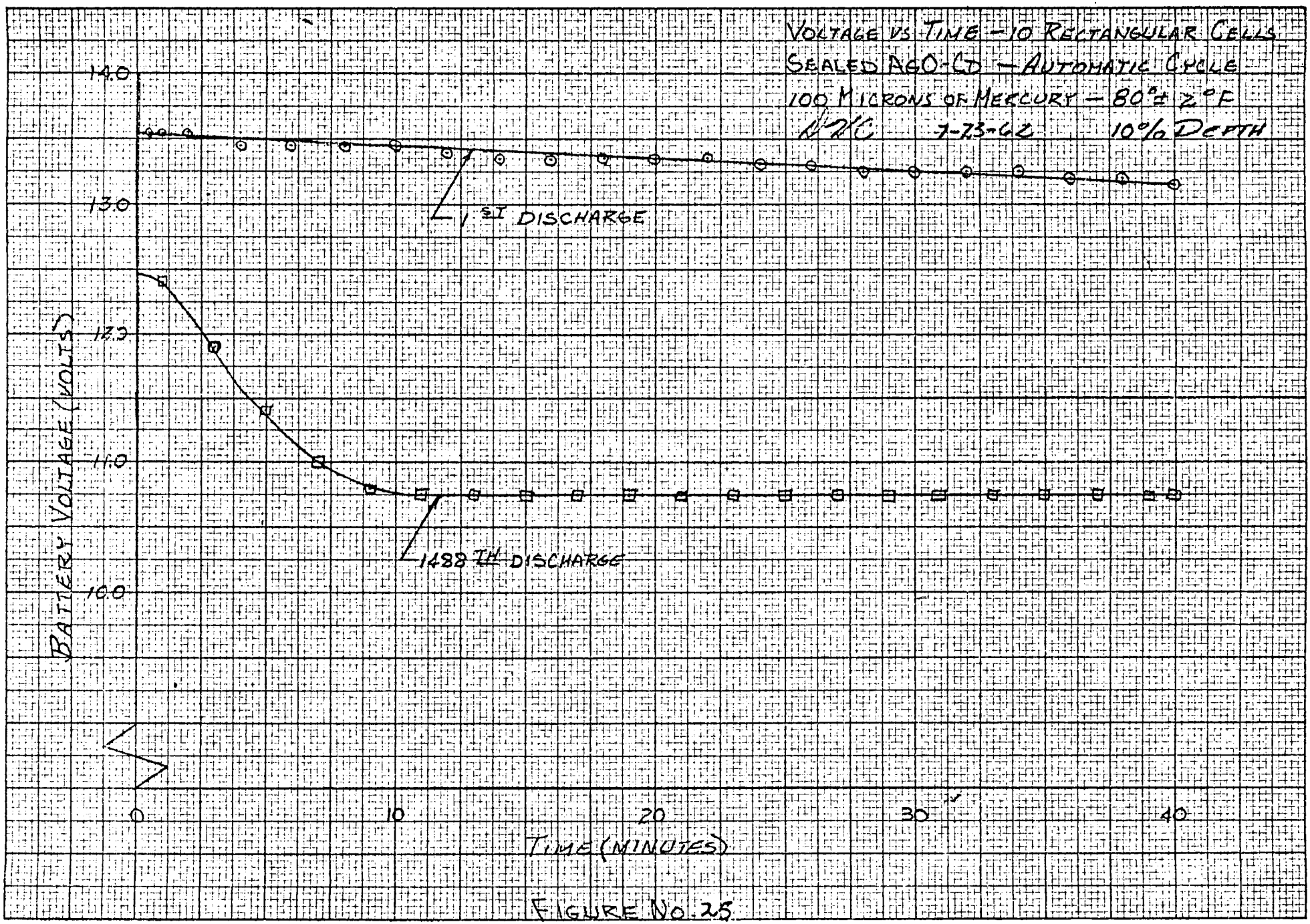

FIGURE No. 25

K&E 10 X 10 TO THE ½ INCH KEUFFEL & ESSER CO. 359-11 MADE IN U.S.A.

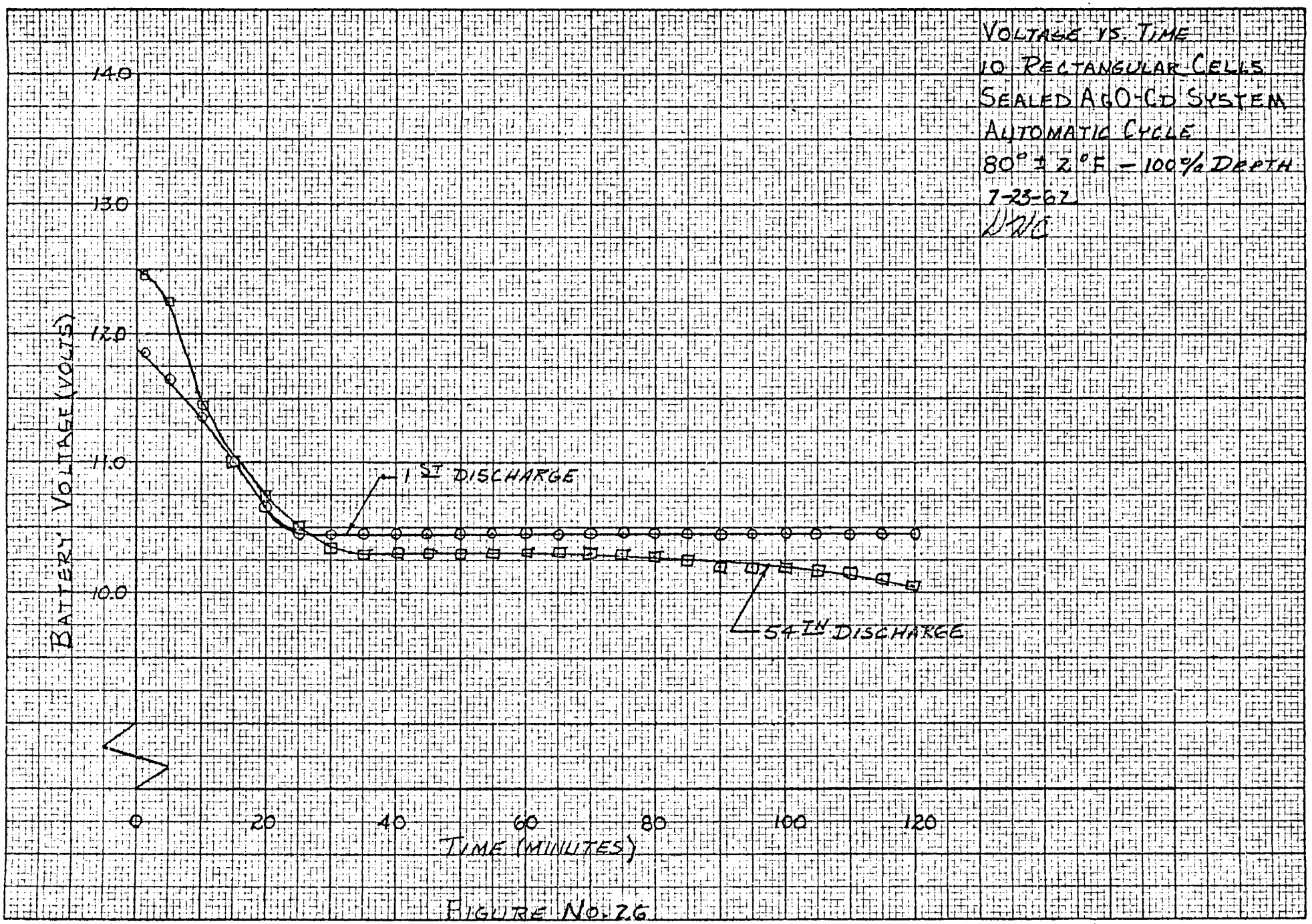

FIGURE No. 26

TABLE NO. XV

CYCLE LIFE VOLTAGE CHARACTERISTICS AT
DISCHARGE DEPTH OF 10%, 20° F

(End-of-Charge and End-of-Discharge Cell Voltage)

Cycle No.	46	47	48	49	50	51	52	53	54	54
1	1.50	1.49	1.50	1.49	1.51	1.50	1.50	1.51	1.49	1.50
	1.08	1.08	1.08	1.08	1.08	1.09	1.08	1.08	1.08	1.08
204	1.50	1.50	1.50	1.50	1.50	1.51	1.49	1.50	1.50	1.49
	1.08	1.08	1.08	1.08	1.07	1.08	1.08	1.08	1.08	1.08
403	1.50	1.51	1.50	1.50	1.50	1.50	1.51	1.51	1.51	1.50
	1.07	1.06	1.07	1.07	1.06	1.07	1.07	1.07	1.07	1.06
605	1.50	1.50	1.50	1.50	1.49	1.49	1.50	1.51	1.51	1.50
	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06
807	1.50	1.51	1.49	1.50	1.50	1.49	1.49	1.51	1.51	1.50
	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06
1007	1.49	1.51	1.49	1.49	1.49	1.50	1.50	1.51	1.51	1.50
	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05
1211	1.50	1.51	1.50	1.50	1.50	1.50	1.50	1.51	1.50	1.50
	1.06	1.05	1.05	1.06	1.05	1.05	1.05	1.05	1.05	1.05
1400	1.50	1.51	1.50	1.50	1.50	1.50	1.50	1.51	1.50	1.50
	1.05	1.06	1.06	1.05	1.05	1.05	1.06	1.06	1.05	1.05
1602	1.50	1.51	1.49	1.49	1.50	1.50	1.50	1.51	1.50	1.50
	1.05	1.05	1.05	1.05	1.05	1.06	1.05	1.05	1.05	1.05
1803	1.51	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.51	1.50
	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05
2007	1.50	1.50	1.49	1.49	1.50	1.49	1.50	1.50	1.50	1.50
	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05
2136	1.50	1.50	1.49	1.49	1.50	1.49	1.50	1.50	1.50	1.50
	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05

TABLE NO. XVI

CYCLE LIFE VOLTAGE CHARACTERISTICS AT DISCHARGE DEPTH OF 10%, 120° F

(End-of-Charge and End-of-Discharge Cell Voltage)

Cycle No.	36	37	38	39	40	41	42	43	44	45
1	1.50	1.52	1.49	1.51	1.48	1.50	1.50	1.49	1.52	1.49
	1.12	1.12	1.12	1.11	1.12	1.11	1.12	1.12	1.12	1.12
102	1.49	1.54	1.48	1.53	1.48	1.52	1.49	1.48	1.54	1.47
	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10
267	1.48	1.61	1.44	1.60	1.44	1.59	1.48	1.46	1.65	1.44
	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10
305	1.64	1.46	1.44	1.46	1.46	1.66	1.66	1.45	1.45	1.44
	1.09	1.10	1.10	1.10	1.10	1.09	1.10	1.10	1.10	1.09
406	1.44	1.64	1.44	1.58	1.62	1.63	1.44	1.44	1.44	1.43
	1.10	1.08	1.10	1.08	1.07	1.06	1.10	1.10	1.10	1.10
493	1.43	1.64	1.44	1.44	1.43	1.59	1.64	1.44	1.59	1.44
	1.09	1.09	1.10	1.09	1.09	1.07	1.08	1.09	1.07	1.10
609	1.43	1.64	1.43	1.45	1.57	1.28	1.56	1.44	1.57	1.64
	1.09	1.09	1.09	1.08	1.04	1.07	1.07	1.09	1.09	1.04

TABLE NO. XVII

CYCLE LIFE VOLTAGE CHARACTERISTICS AT
DISCHARGE DEPTH OF 10%, 80° F

(End-of-Charge and End-of-Discharge Cell Voltage)

Cycle No.	11	12	13	14	15	16	17	18	19	20
18	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08
204	1.50	1.49	1.51	1.50	1.50	1.49	1.50	1.51	1.50	1.50
	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08
408	1.51	1.51	1.50	1.49	1.50	1.49	1.50	1.50	1.50	1.50
	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08
601	1.51	1.51	1.51	1.49	1.50	1.49	1.49	1.50	1.51	1.49
	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08
803	1.49	1.50	1.51	1.50	1.50	1.50	1.49	1.51	1.50	1.50
	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08
1007	1.49	1.50	1.51	1.50	1.50	1.50	1.50	1.51	1.49	1.50
	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08
1211	1.49	1.50	1.51	1.50	1.50	1.50	1.50	1.51	1.49	1.50
	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08
1400	1.50	1.49	1.51	1.50	1.50	1.50	1.50	1.51	1.49	1.50
	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08
1599	1.49	1.49	1.50	1.51	1.49	1.51	1.51	1.51	1.49	1.50
	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08
1699	1.49	1.49	1.51	1.51	1.50	1.50	1.50	1.50	1.51	1.49
	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08

TABLE NO. XVIII

CYCLE LIFE VOLTAGE CHARACTERISTICS AT DISCHARGE DEPTH OF 100%, 80° F

(End-of-Charge and End-of-Discharge Cell Voltage)

Cycle No.	1	2	3	4	5	6	7	8	9	10
1	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.51	1.49	1.50
	1.04	1.04	1.04	1.03	1.04	1.04	1.04	1.04	1.03	1.04
24	1.50	1.49	1.50	1.51	1.52	1.49	1.51	1.50	1.50	1.49
	1.04	1.03	1.04	1.03	1.04	1.03	1.04	1.04	1.04	1.04
48	1.49	1.48	1.49	1.53	1.52	1.48	1.52	1.50	1.50	1.53
	1.03	1.02	1.03	1.04	1.04	1.00	1.03	1.03	1.03	1.03
72	1.49	1.54	1.47	1.54	1.48	1.47	1.55	1.54	1.53	1.50
	1.03	1.02	1.03	1.00	1.03	1.01	1.02	1.02	1.01	1.03
121	1.49	1.54	1.48	1.47	1.49	1.48	1.51	1.54	1.48	1.53
	1.02	1.02	1.01	1.01	1.03	1.01	1.02	1.03	1.02	1.02
146	1.53	1.48	1.47	1.53	1.50	1.48	1.52	1.53	1.52	1.52
	1.03	1.01	1.01	1.02	1.03	1.03	1.03	1.01	1.03	1.00

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